



Short communication

Performance of vapor-fed direct dimethyl ether fuel cell utilizing high temperature polybenzimidazole polymer electrolyte membrane

Jay Neutzler^{a,*}, Guoqing Qian^b, Kevin Huang^a, Brian Benicewicz^b^a University of South Carolina, Department of Mechanical Engineering, 300 Main Street, Columbia, SC 29208, USA^b University of South Carolina, Department of Chemistry and Biochemistry, 541 Main Street, Columbia, SC 29208, USA

H I G H L I G H T S

- ▶ Direct reaction DME produced notable power utilizing PBI membrane.
- ▶ Performance increases with increasing temperatures of 180 °C–210 °C.
- ▶ Performance increases more notably more from 100 to 200 kPa, than 200–300 kPa.
- ▶ Humidification effects were less critical and may provide additional benefits.
- ▶ A peak power density of 129 mW cm^{−2} was achieved at 210 °C and 300 kPa.

A R T I C L E I N F O

Article history:

Received 2 May 2012

Received in revised form

11 June 2012

Accepted 12 June 2012

Available online 19 June 2012

Keywords:

Dimethyl ether

Polybenzimidazole

PEM

Fuel cell

Synthetic fuel

Performance

A B S T R A C T

There is increasing interest in dimethyl ether (DME) as a synthetic fuel. It has present-day relevance and introduces an effective path forward as an energy-dense, low-pressure hydrogen carrier/storage fuel for fuel cells with applications in transportation, stationary, and portable power. Direct reaction DME fuel cells have particular relevance to portable power. This study presents the performance of the vapor-fed direct reaction of DME using high temperature Polybenzimidazole (PBI) Polymer Electrolyte Membrane (PEM). Catalyzed PBI membrane utilized a Pt/Ru black anode and a Pt/C supported cathode. Performance was evaluated from temperatures of 180 °C–210 °C and at pressures from 100 kPa to 300 kPa. A strong performance correlation was observed in this study for these temperatures and pressures. A peak power density of 50 mW cm^{−2} was achieved at 180 °C without back pressure, whereas, an increase to 129 mW cm^{−2} was achieved at 210 °C at 300 kPa pressure.

The performance of high temperature PBI PEMFCs with direct vapor-fed DME are investigated with emphasis on the critical variables of cell operation; temperature, back pressure, and humidity.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Dimethyl ether (DME – CH₃OCH₃) is a “hydrogen carrier” and hydrogen storage medium which possesses many advantages over pure hydrogen, natural gas, gasoline, diesel, methanol, or solid or chemical hydrides. DME is safe, easy to contain, and environmentally friendly. It will readily decay in the atmosphere in 5 days [1]. DME is non-toxic, non-carcinogenic, non-teratogenic (won't interrupt, harm, or alter a developing fetus), and non-mutagenic. It is contained in liquid form at low pressure (~620 kPa), alleviating the high pressure storage issue prevalent with hydrogen (34.5–69.0 MPa). DME is commonly used as a propellant in simple

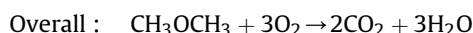
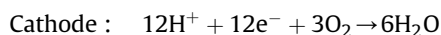
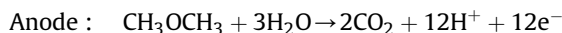
everyday aerosol cans, and as such, does not have shipping transportation issues. DME is a clear gas with a distinctive odor that requires no additional odorant and burns with a visible clean blue flame. It is a fuel that may be efficiently derived from a variety of feed stocks, such as, natural gas, biomass, coal, heavy oil residue, or industrial waste. Production and economic analysis has shown DME to be cost competitive with gasoline, diesel, methanol, and ethanol [2]. DME may be utilized in present-day diesel engines with equivalent centane number making it a promising alternative fuel for prompt implementation [2–6].

DME has been considered for producing a high yield hydrogen supply by reforming. Hydrogen rich gas may be produced through partial oxidation of DME at 600–750 °C with a hydrogen yield of 90% [7]. Although an endothermic process, steam reforming has been demonstrated with 100% DME conversion producing 71 vol % concentration hydrogen at 290 °C [8]. Steam

* Corresponding author. Tel.: +1 832 498 1230 (mobile); fax: +1 803 777 8100.
E-mail address: neutzler@email.sc.edu (J. Neutzler).

reformation catalysts have been examined to increase the flow production rates and evaluated for temperatures and yield [9,10]. This is a viable path for DME use, however, reformers may be too large, complex, or costly when considering smaller portable power situations. Direct DME reaction may have advantages when portability is a key requirement.

DME ($\text{CH}_3\text{—O—CH}_3$) has no carbon–carbon bonds, and as such, requires less activation energy to react which affords relatively high performance as a direct reaction fuel cell. The half-cell and full reactions are;



As shown, the reaction produces 12 electrons (e^-) versus 2 for a pure H_2 (hydrogen) reaction.

Direct oxidation of DME has been performed utilizing low-temperature perfluorosulfonic acid based polymer membrane (e.g., Nafion[®]) fuel cells with relative success. A power density of 120 mW cm^{-2} was achieved with DME in liquid form at 130°C and 500 kPa at 0.4 V [11]. This was similar in performance to Direct Methanol under the same conditions. A recent review of DME progress describes several methods, catalysts, conditions, and results where the highest performance achieved was $\sim 120 \text{ mW cm}^{-2}$ utilizing a Nafion[®] based membrane [12].

Catalyst studies have been performed to explore more optimal anodes. A study of electro-oxidation of DME was performed by Liu et al. [13] on carbon supported platinum (Pt/C) and carbon supported binary catalysts (PtMe/C, where Me = Ru, Sn, Mo, Cr, Ni, Co, and W). In sulfuric acid half-cell tests, they found that PtRu/C (1:1 M ratio) had the best electro-catalytic activity at the lower potentials (i.e., $<0.55 \text{ V}$) over the other test specimens. They also determined that the DME oxidation reaction (DOR) performance had higher temperature dependence than Methanol oxidation reaction (MOR) in the 30°C – 60°C range that was tested. Recently, a Pt-to-Ru ratio study was performed utilizing DME Fuel Cells with Nafion[®] 117 membranes [14]. The peak performances were found with unsupported Pt₈₀Ru₂₀, Pt₆₇Ru₃₃, and Pt₅₀Ru₅₀ M ratios at 80°C .

DME performance testing has been conducted on intermediate-temperature (650°C – 850°C) Solid Oxide Fuel Cells resulting in considerably higher power densities (965 mW cm^{-2} at 850°C and 187 mW cm^{-2} at 650°C) utilizing a Ni-YSZ anode catalyst [15]. However, the performance degraded quickly (a reduction of $\sim 9.7\%$ in 300 min at 850°C), which limits its application.

Phosphoric acid doped polybenzimidazole (PBI) was reported as a promising candidate for a high temperature PEM material [16–19]. It was shown that this polymer electrolyte membrane exhibited high proton conductivity at temperatures up to 200°C , low reactant permeability, high fuel impurity tolerance, excellent oxidative and thermal stability, and nearly zero water drag coefficient. Direct alcohol (vapor-fed) fuel cells with PBI membrane have recently been reported. Direct Ethanol PBI fuel cells were tested at temperatures of 125°C , 150°C , 175°C , and 200°C with oxygen cathode supply [20]. Peak power output occurred at 200°C producing $\sim 70 \text{ mW cm}^{-2}$. Direct Methanol PBI fuel cells have also been tested at the same temperatures resulting in a peak power of 139 mW cm^{-2} at 200°C [21].

A recent international patent was published describing a method of operating a direct DME fuel cell with a PBI membrane and recently reported [22,23]. Anode catalyst loadings of Pt/Ru (2:1) on carbon black (1.5 mg cm^{-2} of Pt/Ru) were utilized with

a cathode of 0.7 mg cm^{-2} of Pt and 0.3 mg cm^{-2} of PBI additive. Performance polarization curves were recorded and peak powers were tabulated at 150°C , 175°C , 200°C , 225°C , and 250°C reported as 12, 29, 52, 78, and 96 mW cm^{-2} , respectively. However, it was also stated that after an hour of operation at 200°C , the maximum power increased to 100 mW cm^{-2} (vs. 52 mW cm^{-2}). Although pressure and humidification aspects were mentioned, very little data or supporting figures were presented.

Direct vapor-fed DME Fuel Cells based on phosphoric acid-PBI membranes have not been sufficiently reported to date. The performance of high temperature PBI PEMFCs with direct vapor-fed DME are investigated with emphasis on the critical variables of cell operation; temperature, back pressure, and humidity.

2. Experimental

Typical Membrane Electrode Assemblies (MEAs) were prepared using para-PBI membrane with a phosphoric acid doping level of 22 mol of phosphoric acid per mole of polymer repeat unit [24]. The anode (Alfa Aesar) was a Pt/Ru black (1:1 M) with a total precious metal loading of 4 mg cm^{-2} (Pt: 2.7 mg cm^{-2} , Ru: 1.3 mg cm^{-2}) on Toray carbon paper. The cathode was 1 mg cm^{-2} Pt/carbon supported on carbon cloth (BASF Fuel Cell, Inc.). Both anode and cathode electrodes had micro-porous layers on the Gas Diffusion Layer (GDL). The MEA was assembled and hot-pressed at 140°C for 120 s. The MEA was mounted in a 10 cm^2 Fuel Cell Technologies single cell test fixture. The cell was tested on a Fuel Cell Technologies test station (Model: 120A2M). Resistance values were taken on an Agilent 4338B Ohmmeter at 1000 Hz. The cell “break-in” duration was for 24 h (minimum) on dry hydrogen/air with flows of 50/83 sccm at 180°C . For DME testing, dry cathode air flow was provided at 83 sccm minimum and 3.3 stoic thereafter. The anode DME flow was constant at 60 sccm (6 sccm cm^{-2}), directed through a humidifier (Fuel Cell Technologies Model: DAFS), and typically humidified at a temperature and pressure to achieve a 3:1 steam to DME ratio. Two main test factors were considered for DME performance tests: operational temperature at 3 levels (180°C , 195°C , 210°C) and operational pressures at 3 levels (100 kPa, 200 kPa, 300 kPa). Polarization scans of constant voltage were performed from 0.7 V to 0.15 V and back at 50 mV steps with 30 s dwell per step.

3. Results and discussion

3.1. Fuel cell performance

Fig. 1 shows the polarization curves for PBI membrane fuel cells operated on both hydrogen and DME at various conditions. The polarization curve of a Nafion[®] based fuel cell operating on DME is also included for comparison [14]. After break-in, the cell performance of the para-PBI membrane was similar to that reported earlier for a membrane with similar composition [24]. The DME open circuit potential ($V_{\text{OC}} \approx 0.7 \text{ V}$) was approximately 200 mV lower than for pure hydrogen ($V_{\text{OC}} \approx 0.9 \text{ V}$) likely reflecting the degree of DME being reformed into simple fuels in the anode chamber. Overall, the performance of the Direct DME/PBI fuel cell was relatively high when compared with state-of-the-art Direct DME/Nafion[®] or Direct Methanol/Nafion[®] based systems, even when operating on lower anode and cathode Pt loading levels. Over the test conditions examined in this study, the peak power densities ranged from 50 mW cm^{-2} which was achieved at 180°C and 100 kPa, to 129 mW cm^{-2} which was achieved at 210°C and 300 kPa.

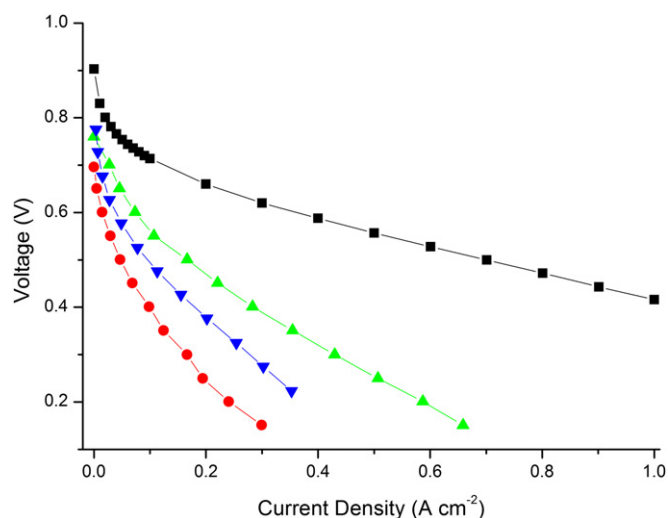


Fig. 1. Polarization curves for PBI fuel cells operated on hydrogen and DME. Literature data for Nafion fuel cells operated on DME are provided for comparison. (PBI fuel cell – anode: Pt/Ru black, 4 mg cm⁻²; cathode: Pt/C, 1 mg cm⁻², (■) H₂/air 180 °C 100 kPa abs., (●) DME/air 180 °C 100 kPa abs., (▲) DME/air 210 °C 300 kPa abs.; Nafion® 117 fuel cell [14] – anode: Pt/Ru black, 6 mg cm⁻², cathode: Pt black, 4 mg cm⁻², (▼) DME/air, 80 °C 300 kPa abs.).

3.2. Effects of temperature and pressure

Additional investigations of the fuel cell performance were performed at temperatures of 180 °C, 195 °C, and 210 °C, and at operational pressures of 100 kPa, 200 kPa, and 300 kPa using a 3 × 3 test matrix to explore the fuel cell performance on these variables. Fig. 2 shows the polarization curves and power densities of direct DME fuel cells with zero back pressure at 180 °C, 195 °C, and 210 °C. It can be seen that the performance of this type fuel cell is highly temperature dependent with an approximately 2X increase in voltage at 0.3 A cm⁻² or a doubling of the voltage across most of the current density range when the temperature was raised from 180 °C to 210 °C. This could be explained by the faster DME oxidation reaction at higher operational temperatures.

Fig. 3 shows the effects back pressure on the performance of direct DME fuel cells operated at 210 °C. The power density and polarization curves are shown at 210 °C across the selected

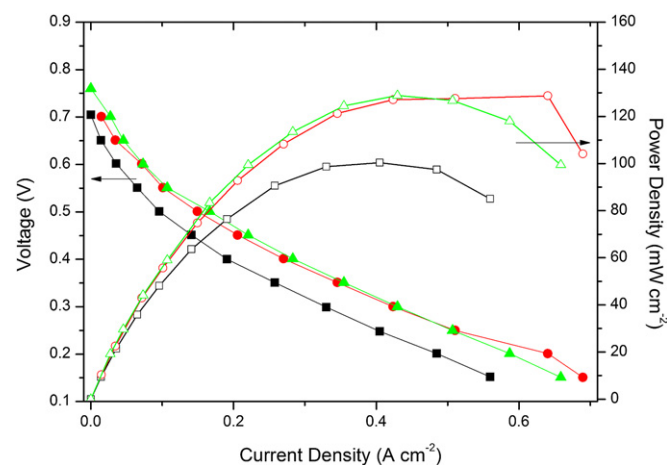


Fig. 3. Polarization curves and power densities of direct DME PBI fuel cells at 210 °C and various pressures. (PBI fuel cell – anode: Pt/Ru black, 4 mg cm⁻²; cathode: Pt/C, 1 mg cm⁻², DME/air, 210 °C, at (■) 100 kPa, (●) 200 kPa, (▲) 300 kPa abs.).

pressures. Fuel cell performance increased with increased pressure, more notably from 100 kPa to 200 kPa than from 200 kPa to 300 kPa. This was also observed at 195 °C and 180 °C (not shown). This non-Nernstian behavior was observed over all the experimental conditions conducted in this study and strongly suggests a mass transport limitation at atmospheric pressures. This limitation was apparently overcome at pressures of 200 kPa and above, and further increases in pressure (e.g., 200 kPa–300 kPa) did not provide an appreciable increase in fuel or water transport or increase in performance.

3.3. Effects of fuel humidity

Further testing was performed to evaluate different steam-to-fuel ratios. The anode humidifier temperature was adjusted to provide steam-to-fuel ratios as follows for the ambient pressure case; 95 °C for 5:1 (83% RH), 92 °C for 3:1 (75% RH), and 85 °C for 1.33:1 (57% RH). As seen in Fig. 4, the performance in the low current density region was similar at the different steam-to-fuel ratios. At higher current densities, an apparent mass transport limitation effect was observed. The different experimental conditions used in this study were created by adding more water to

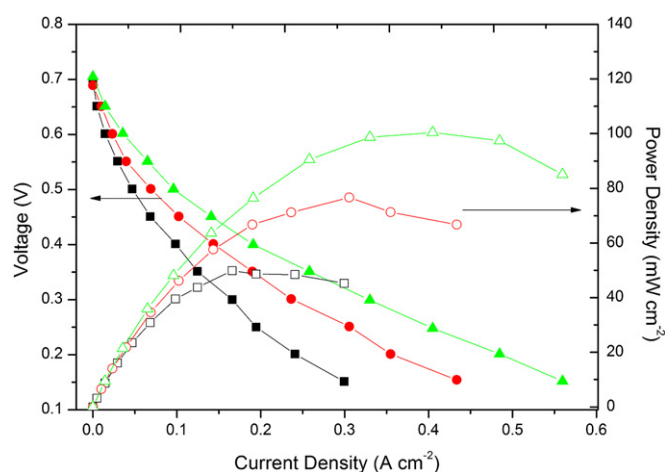


Fig. 2. Temperature dependence of direct DME PBI fuel cells at 100 kPa abs (PBI fuel cell – anode: Pt/Ru black, 4 mg cm⁻²; cathode: Pt/C, 1 mg cm⁻², DME/air, 100 kPa abs., at (■) 180 °C, (●) 195 °C, (▲) 210 °C).

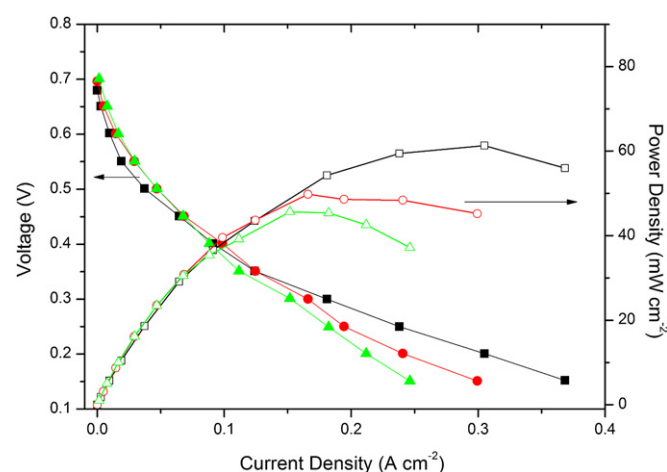


Fig. 4. Effects of relative humidity on the performance of direct DME PBI fuel cells at 180 °C, 100 kPa abs. (PBI fuel cell – anode: Pt/Ru black, 4 mg cm⁻²; cathode: Pt/C, 1 mg cm⁻², DME/air, 180 °C, 100 kPa abs., at R.H. (■) 57%, (●) 75%, (▲) 83%).

a constant DME flow. Thus, higher RH conditions diluted the fuel concentration which likely caused the mass transport limitations. This result could be beneficial in the design of practical systems. If the only water requirement is to supply sufficient water as described in the anode half reaction, then fuel concentration can be maximized and water management problems greatly alleviated. This may lead to a more robust design for a Direct DME fuel cell.

4. Conclusions

Direct DME fuel cells utilizing PBI membranes produced significant power densities at moderate catalyst loadings when operating at high temperatures. It was shown in this study that there was a strong correlation of operating temperature and pressure with fuel cell performance. A peak power density of 50 mW cm^{-2} was achieved at 180°C and 100 kPa pressure, whereas an increase to 129 mW cm^{-2} was achieved at 210°C and 300 kPa. A slight increase in pressure resulted in a significant increase in performance, although further increases in pressure did not appear necessary for obtaining high performance. The investigation of humidification effects showed that this variable was less critical than low-temperature membrane operation and may provide additional benefits in system design. Based on the promising aspects of the high temperature PBI membrane Direct DME fuel cell, further investigations are warranted into the development and understanding of anode and cathode catalysts, GDL optimization, fuel utilization effects, as well as long term durability.

Acknowledgments

This work was funded in part by Neutzler & Associates, Inc. from a grant provided by the South Carolina Research Authority (SCRA; 2011-01-06) Greater Columbia Fuel Cell Challenge. This work was also partially supported by BASF Fuel Cell, Inc and DARPA (W91CRB-10-1-0007).

References

- [1] D.A. Good, Atmospheric Fate of Dimethyl and Fluorinated Ethers, Purdue University, 1999.

- [2] T.H. Fleisch, R.A. Sills, M.D. Brisco, *Journal of Natural Gas Chemistry* 11 (2002) 1–14.
- [3] A.M. Rouhi, *Chemical & Engineering News* 73 (1995) 37–39.
- [4] T.H. Fleisch, A. Basu, M.J. Gradassi, J.G. Masin, Dimethyl ether: a fuel for the 21st century, in: M.d. Pontes, R.L. Espinoza, C.P. Nicolaides, J.H. Scholtz, M.S. Scurrell (Eds.), *Studies in Surface Science and Catalysis*, vol. 107, Elsevier, 1997, pp. 117–125.
- [5] S.E. Plotkin, *Assessment of PNGV Fuels Infrastructure: Infrastructure Concerns Related to the Safety of Alternative Fuels*, Argonne National Laboratory, 2000.
- [6] T.A. Semelsberger, R.L. Borup, H.L. Greene, *Journal of Power Sources* 156 (2006) 497–511.
- [7] Q. Zhang, X. Li, K. Fujimoto, K. Asami, *Applied Catalysis A: General* 288 (2005) 169–174.
- [8] V.V. Galvita, G.L. Semin, V.D. Belyaev, T.M. Yurieva, V.A. Sobyenin, *Applied Catalysis A: General* 216 (2001) 85–90.
- [9] K. Takeishi, H. Suzuki, *Applied Catalysis A: General* 260 (2004) 111–117.
- [10] T.A. Semelsberger, K.C. Ott, R.L. Borup, H.L. Greene, *Applied Catalysis B: Environmental* 65 (2006) 291–300.
- [11] J.T. Muller, P.M. Urban, W.F. Holderich, K.M. Colbow, J. Zhang, D.P. Wilkinson, *Journal of the Electrochemical Society* 147 (2000) 4058–4060.
- [12] A. Serov, C. Kwak, *Applied Catalysis B: Environmental* 91 (2009) 1–10.
- [13] Y. Liu, S. Mitsushima, K.-I. Ota, N. Kamiya, *Electrochimica Acta* 51 (2006) 6503–6509.
- [14] P. Zelenay, in: 2011 Hydrogen Program Annual Merit Review and Peer Evaluation Meeting, Arlington, VA, 2011.
- [15] C. Su, R. Ran, W. Wang, Z. Shao, *Journal of Power Sources* 196 (2011) 1967–1974.
- [16] J.T. Wang, R.F. Savinell, J. Wainright, M. Litt, H. Yu, *Electrochimica Acta* 41 (1996) 193–197.
- [17] L. Xiao, H. Zhang, E. Scanlon, L.S. Ramanathan, E.-W. Choe, D. Rogers, T. Apple, B.C. Benicewicz, *Chemistry of Materials* 17 (2005) 5328–5333.
- [18] J. Mader, L. Xiao, T.J. Schmidt, B.C. Benicewicz, Polybenzimidazole/acid complexes as high-temperature membranes, in: G. Scherer (Ed.), *Adv. Polym. Sci., Fuel Cell II*, vol. 216, Springer GmbH, 2008, pp. 63–124.
- [19] D.C. Seel, B.C. Benicewicz, L. Xiao, T.J. Schmidt, High-temperature polybenzimidazole-based membranes, in: W. Vielstich, H.A. Gasteiger, H. Yokikawa (Eds.), *Handbook of Fuel Cells: Advances in Electrocatalysis, Materials, Diagnostics and Durability*, vol. 5, John Wiley & Sons Ltd, 2009, pp. 300–312.
- [20] J. Lobato, P. Canizares, M.A. Rodrigo, J.J. Linares, R.N. Lopez-Vizcaino, *Energy & Fuels* 22 (2008) 3335–3345.
- [21] J. Lobato, P. Cañizares, M.A. Rodrigo, J.J. Linares, *Fuel Cells* 9 (2009) 597–604.
- [22] WO 2011/035784 A1 J.O. Jensen, Q. Li, N.J. Bjerrum, T. Steenberg, Method of Operating a Direct Dimethyl Ether Fuel Cell System, Danmarks Tekniske Universitet - DTU, Den, 2011.
- [23] J.O. Jensen, A. Vassiliev, M.I. Olsen, Q.F. Li, C. Pan, L.N. Cleemann, T. Steenberg, H.A. Hjuler, N.J. Bjerrum, *Journal of Power Sources* 211 (2012) 173–176.
- [24] S. Yu, H. Zhang, L. Xiao, E.W. Choe, B.C. Benicewicz, *Fuel Cells* 9 (2009) 318–324.